APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. 2005; **19**: 879–886
Published online 9 May 2005 in Wiley InterScience (www.interscience.wiley.com). DOI:10.1002/aoc.904

Microwave-assisted synthesis and insecticidal properties of biologically potent organosilicon(IV) compounds of a sulfonamide imine

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Received 5 January 2005; Revised 16 January 2005; Accepted 26 January 2005

Microwave-assisted synthesis and spectroscopic studies of dimethyl-, diphenyl- and triphenylsilicon(IV) chelates derived from the reactions of organochlorosilanes with the sodium salt of a biologically active nitrogen donor ligand N∩NH are described. The resulting products have been isolated and characterized by elemental analyses, molecular weight determinations and conductance measurements. On the basis of electronic, infrared, ^{1}H, ^{13}C and ^{29}Si NMR spectral studies, trigonal bipyramidal and octahedral geometries have been suggested for the resulting complexes. The biological activity of the ligand and its corresponding complexes has been examined with regard to antifungal and antibacterial activity against pathogenic fungi and bacteria, and the results are quite encouraging. All the compounds have also been found to act as nematicides and insecticides, by reducing the number of nematodes (*Meloidogyne incognita*) and insects (*Trogoderma granarium*).

KEYWORDS: microwave synthesis; insecticidal activity; pesticidal activity; organosilicon(IV) complexes

INTRODUCTION

Chemical processes are as old as time, and over the centuries chemists have been trying to understand natural processes to develop methods based on the philosophies that are nature's very own. In the context of chemistry, sustainability deals with the question of how syntheses can be performed safely with minimum input of energy and other resources and at the same time reducing waste and by-products.

Microwave energy generates rapid intense heating of polar substances with significant reductions of reaction times, cleaner reactions and, in many cases, higher yields. The main advantage of microwave heating is the almost instantaneous 'in-core' heating of materials in an homogeneous and selective manner, coupled with the significantly shorter reaction times that can be achieved. This implies a considerable saving in energy. The synthesis of a number of B-metal compounds has been accomplished in pressure vessels similar to those used in high pressure organic syntheses.[1] Large reaction rate increases of up to 40 times were observed relative to the conventionally heated samples, and for comparable yields.

Organometallic and coordination compounds have received surprisingly little attention by microwave chemists, relative to other areas of study, despite indications that improved syntheses may result here, too. In particular, nothing has been reported so far on the synthesis of organosilicon derivatives incorporating the N∩NH moiety using microwave irradiation. The importance of microwave technology and the versatile pharmacological activity of organosilicon compounds prompted us to report for the first time a microwave-assisted method for the synthesis of some new biologically potent organosilicon complexes.

The results of these investigations seem to be promising. The ligand selected for these studies is shown in Fig. 1.

EXPERIMENTAL

All the chemicals and solvents used were dried, distilled and purified by standard methods. Adequate care was taken to keep the organosilicon(IV) complexes, chemicals

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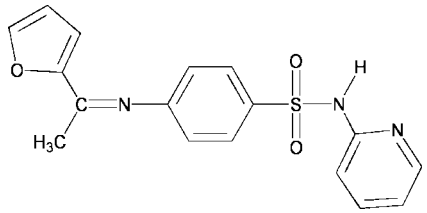

Figure 1. Structure of Sulfonamide imine ligand used.

and glass apparatus free from moisture. Clean and well-dried glass apparatus fitted with Quickfit interchangeable standard ground joints was used throughout the experimental work. Moisture was excluded from the glass apparatus using calcium chloride drying tubes.

Preparation of the ligand sulfonamide imine

The ligand was prepared by the condensation of alcoholic 2-acetylfuran (2.25 g) with alcoholic sulfathiazole (5.10 g) in an open 100 ml borosil beaker. The reaction mixture was irradiated for 5 min in a microwave oven at 700 W till the completion of the reaction. Later, the ligand was dried and then recrystallized from Ethyl alcohol (35 ml) and again dried under reduced pressure. Thus, the ligand was prepared under economical, safe and environmentally ecofriendly condition. This method also saved reaction time and is an attractive alternative to the presently used methods with large amounts of solvent and much time. The physical properties and microanalysis of this sulfonamide imine is recorded in Table 1.

Preparation of the organosilicon(IV) complexes

For the synthesis of these complexes, di- and tri-organosilicon chloride (Ph_2SiCl_2, Me_2SiCl_2, or Ph_3SiCl) (0.64–0.50 g, 0.72–0.77 g, or 0.65 g) and the sodium salt of the sulfonamide imine (prepared by adding the corresponding weight of sodium to the sulfonamide imine in 5 ml dry methanol) in 1 : 1 and 1 : 2 molar ratios were irradiated inside a microwave oven at 700 W for about 5–8 min. The products were recovered from the microwave oven and dissolved in few millilitres of dry methanol; the white precipitate of sodium chloride formed during the course of the reaction was removed by filtration and the filtrate was dried under reduced pressure. The resulting product was repeatedly washed with petroleum ether and then finally dried at 40–60 °C/0.5 mmHg for 3–4 h. The purity was further checked by thin-layer chromatography using silica gel-G. The details of these reactions and the analyses of the resulting products are recorded in Table 1.

Analytical methods and physical measurements

Carbon and hydrogen analyses were performed at the microanalytical laboratory of CDIR Lucknow. Nitrogen and sulfur were estimated by the Kjeldahl and Messenger methods respectively. Silicon was estimated gravimetrically as SiO_2. Conductivity was measured at 32 ± 1 °C with a conductivity bridge (type 305 Systronics model) and molecular weights were determined by the Rast camphor method. Infrared spectra were recorded on a Perkin–Elmer 577 grating spectrophotometer in the range 4000–200 cm^{-1}, as Nujol mulls using KBr optics. ^1H NMR spectra were recorded in DMSO-d_6 on a Bruker AM 270 spectrometer. ^{13}C and ^{29}Si NMR spectra were recorded in methanol using tetramethylsilane (TMS) as an internal standard on the same spectrometer.

The linear growth method[2] for antifungal activity, paper-disc plate method[3,4] for antibacterial activity, and step-by-step method[5] for obtaining quantities of clean *Meloidogyne*

Table 1. Details of reactions between sulfonamide imine with organosilicon chloride

Sulfonamide imine and product formed[a]	Formula, colour and state	Yield (%)	M.p. (°C)	Elemental analysis (%) C Found (Calc.)	H Found (Calc.)	N Found (Calc.)	S Found (Calc.)	Si Found (Calc.)	Cl Found (Calc.)	Mol. wt Found (Calc.)
($N^{\cap}NH$)	$C_{17}H_{15}N_3O_3S$	92	138–140	59.56	4.30	12.04	9.10	—	—	316
	Brown solid			(59.80)	(4.42)	(12.30)	(9.39)			(341.39)
$Me_2SiCl(N^{\cap}N)$	$C_{19}H_{20}N_3O_3SSiCl$	91	84–86	52.19	4.33	9.40	7.11	6.18	7.86	418
	Sandy brown solid			(52.80)	(4.64)	(9.68)	(7.38)	(6.47)	(8.16)	(433.99)
$Me_2Si(N^{\cap}N)_2$	$C_{36}H_{34}N_6O_6S_2Si$	95	121–123	58.24	4.29	11.10	8.39	3.58	—	718
	Cream solid			(58.51)	(4.63)	(11.37)	(8.67)	(3.80)		(738.92)
$Ph_2SiCl(N^{\cap}N)$	$C_{29}H_{24}N_3OP_3SSiCl$	90	79–81	62.18	4.09	7.18	5.38	4.88	6.04	545
	Brown solid			(62.40)	(4.33)	(7.52)	(5.74)	(5.03)	(6.35)	(558.13)
$Ph_2Si(N^{\cap}N)_2$	$C_{46}H_{38}N_6O_6S_2Si$	97	164–166	63.84	4.21	9.52	7.17	3.04	—	850
	Peach solid			(64.01)	(4.43)	(9.73)	(7.43)	(3.25)		(863.06)
$Ph_3Si(N^{\cap}N)$	$C_{35}H_{29}N_3O_3SSi$	94	169–171	69.78	4.59	6.85	5.03	4.31	—	576
	Yellow–brown solid			(70.08)	(4.87)	(7.00)	(5.34)	(4.68)		(599.78)

[a] ($N^{\cap}NH$) = 2-acetylfuran sulfapyridine.

incognita eggs were followed. Other methods used for biological activity are as described below.

Rearing of the experimental insects

Insects were reared according to a literature procedure.[6] The stock culture was established in the laboratory on disinfested wheat grains in large presterilized glass jars. Inside the jars, 100 pairs of fresh insects were released on disinfested wheat grains. Healthy conditions of the stock culture were maintained by frequent replacement of stale grains with fresh ones. The stock and subculture were provided with optimum condition of temperature and relative humidity in the ranges $35 \pm 2\,^{\circ}C$ and $60 \pm 10\%$ respectively. After the stock culture bloomed to it's youth, subsequent cultures were also established by releasing a few pairs of newly emerged adult beetles on fresh disinfested wheat grains in small glass jars. After allowing 7–8 days for oviposition, beetles were removed. A continuous supply for experimentation was thus maintained by repeating the process every week. Wheat grains were used for stock and for subculture to prevent food effects. To rule out the possibilities of infection, presterilized jars and disinfested grains were used. The insects were transferred with the help of forceps and hair brushes.

Assessment of the toxicity of the chemicals

Ovicidal treatment was completed as described in Refs 7 and 8.

Larvicidal treatment

Larvicidal efficacy of the chemicals was assessed by the feeding method. First instar larvae separated from subculture were kept in vials containing 5 g of topically treated wheat grains with 1 ml of chemicals. Larvae were allowed to continue their development on this diet till pupation. Each dose was replicated three times. The control contained solvent-treated food only. The percentage larvae mortality and percentage corrected mortality were calculated using Abott's formula.[8]

Pupicidal treatment

Last larval instars were sorted out from the subculture and were kept in a separate container on the same rearing medium; pupae of known age (0–12 h) were taken out and were dipped in the desired concentration of the chemicals. Three replicates were set for each dose, along with a control, and after 96 h the total emergence and pupal mortality were recorded. The percentage pupal mortality and pupal corrected mortality were calculated using Abott's formula

Adulticidal treatment

The adulticidal action was assessed by the contact method. 5 g of wheat grains were treated with 1 ml of respective doses. The solvent was allowed to evaporate completely. The experiment was replicated three times, along with a control. Newly emerged adults were taken from the subculture and were released in to plastic vials containing treated food. Observations were taken after 48 h and the percentage corrected mortality was calculated using Abott's formula.

RESULTS AND DISCUSSION[9–15]

The reactions of triphenylchlorosilane, diphenyldichlorosilane, and dimethyldichlorosilane with the sodium salt of monobasic bidentate imine in different stoichiometric proportions resulted in the isolation of $Ph_2SiCl(N^{\cap}N)$, $Me_2SiCl(N^{\cap}N)$, $Ph_3Si(N^{\cap}N)$, $Ph_2Si(N^{\cap}N)_2$ and $Me_2Si(N^{\cap}N)_2$ complexes. These are soluble in common organic solvents and have sharp melting points. The low values of molar conductance ($10–25\ \Omega^{-1}\ cm^2\ mol^{-1}$) show them to be non-electrolytes. The monomeric nature of these complexes was confirmed by molecular weight determinations.

Electronic spectra

The electronic spectra of 2-acetylfuran sulfapyridine and its silicon complexes are given in Table 2. A band due to the >C═N chromophore[16] in the spectrum of the ligand at 365 nm shifts to a lower wavelength in the silicon complexes and appears at 353, 346, 348, 356 and 350 nm in the various 1 : 1 and 1 : 2 products. This clearly indicates the coordination of the azomethine nitrogen to the silicon atom. Further, two bands at 252 nm and 283 nm are due to $\pi-\pi^*$ transitions

Table 2. UV and IR spectral data of sulfonamide imine and its silicon complexes[a]

Sulfonamide imine and product formed	$n-\pi^*\lambda_{max}$/nm >C═N	$\pi-\pi^*\lambda_{max}$/nm C_6H_5 ring	$\pi-\pi^*\lambda_{max}$/nm >C═N	ν(NH)	ν(C═N)	ν(Si ← N)	ν(Si–Cl)
($N^{\cap}NH$)	365	252	283	3420–3110(m)	1630(vs)	—	—
$Me_2SiCl(N^{\cap}N)$	353	267	280	—	1624(vs)	574(w)	420(m)
$Me_2Si(N^{\cap}N)_2$	356	271	277	—	1627(vs)	579(w)	—
$Ph_2SiCl(N^{\cap}N)$	346	276	274	—	1621(vs)	570(w)	436(m)
$Ph_2Si(N^{\cap}N)_2$	350	280	270	—	1615(vs)	572(w)	—
$Ph_3Si(N^{\cap}N)$	348	286	266	—	1619(vs)	565(w)	—

[a] m: medium; vs: very strong; w: weak.

within the benzene ring and (>C═N) band of the azomethine group respectively. The K band $\pi-\pi^*$ showed a red shift due to the overlap of the central metal d-orbital with the p-orbital of the donor atom, which causes an increase in conjugation and the B-band undergoes a hypsochromic shift in the complexes.

Infrared spectra

The medium intensity bands exhibited in the region 3420–3110 cm^{-1} can be assigned to the ν(NH) frequency of the free ligand, which disappear in the silicon complexes, suggesting the possible loss of a proton of the α-nitrogen on complexation of the silicon atom. The >C═N frequency of the free azomethine observed in the region of 1630 cm^{-1} is shifted to the lower frequency region in the case of the complexes.[17] Two new bands in the complexes at 770–745 and 579–565 cm^{-1} are due to ν(Si–C) and ν(Si ← N) respectively,[18] which are absent in the spectrum of the ligand. In the case of $Ph_2SiCl(N^{\cap}N)$- and $Me_2SiCl(N^{\cap}N)$-type of complexes, a band of medium intensity at 436–420 cm^{-1} is due to ν(Si–Cl) vibration.[18]

^{1}H NMR spectra

The proton magnetic resonance spectra of the ligand and its corresponding silicon complexes were recorded in DMSO-d_6 using TMS as the internal standard. The chemical shift values δ (ppm) of the different protons are given in Table 3. For the sake of convenience, the spectra of sulfonamide imine and its 1 : 1 and 1 : 2 silicon complexes are discussed in detail. The broad signal exhibited by the ligand due to the NH proton at δ 10.50 ppm disappears in the silicon derivatives, indicating the coordination of the nitrogen atom. The azomethine proton signal due to the methyl proton (CH_3–C═N) appears at 2.08 ppm in the ligand. The downfield shift of this position in the spectra of the complexes substantiates the coordination of the azomethine nitrogen to the silicon atom. Further, new signals at δ 1.05 ppm and δ 1.16 ppm, in the 1 : 1 and 1 : 2 complexes respectively, are due to the methyl protons of the Me_2Si group. In the spectra of the complexes, a downfield shift in the position of –CH_3 and aromatic protons indicates deshielding, as well as the coordination of azomethine nitrogen to the silicon atom. This is probably due to the donation of the lone pair of electrons by the nitrogen to the central silicon atom, resulting in the formation of a coordinate linkage (Si ← N).

^{13}C NMR spectra

The ^{13}C NMR spectra of sulfonamide imine and its corresponding silicon complexes were also recorded in dry MeOH. A considerable shift (Table 4) in the positions of carbon atoms attached to the different participating groups clearly indicates the bonding of azomethine nitrogen to the silicon atom.

^{29}Si NMR spectra

In the cases of the silicon complexes $Ph_2SiCl(N^{\cap}N)$, $Me_2SiCl(N^{\cap}N)$, $Ph_3Si(N^{\cap}N)$, $Ph_2Si(N^{\cap}N)_2$ and $Me_2Si(N^{\cap}N)_2$, signals at δ–93 ppm, δ–96 ppm, δ–89 ppm, δ–107 ppm and δ–127 ppm respectively are assigned for the penta- and hexa-coordinated states around the silicon atom.

On the basis of the above spectral studies, possible trigonal bipyramidal[19] and octahedral geometries[16] have been suggested for the 1 : 1 and 1 : 2 types of complexes respectively (Figure 2).

Antifungal and antibacterial activity

The results reported in Tables 5 and 6 reveal that the silicon complexes of sulfonamide imine are more active for all the test organisms than the corresponding ligand. The compounds containing a halogen atom attached directly to the silicon atom also showed moderate activity. The mode of action of these compounds may involve the formation of a hydrogen bond through the –N═C group with the active centres of the cell constituents, resulting in an interference with the normal cell processes. Therefore, it might be inferred from the above studies that the introduction of sulfur and silicon in the organic moiety leads to the increased bactericidal and

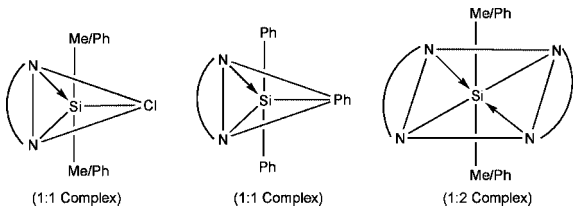

Figure 2. Geometry of the 1 : 1 and 1 : 2 complexes.

Table 3. ^{1}H NMR and ^{29}Si NMR spectral data (δ, ppm) of the sulfonamide imine and its silicon complexes[a]

Sulfonamide imine and product formed	Si–CH_3	CH_3	NH	Aromatic proton	^{29}Si NMR
($N^{\cap}NH$)	—	2.08 (3H, S)	10.50 (br, 1H)	8.00–6.59 (m)	—
$Me_2SiCl(N^{\cap}N)$	1.05 (br, 6H)	2.20 (3H, S)	—	8.30–7.04 (m)	−96
$Me_2Si(N^{\cap}N)_2$	1.16 (br, 6H)	2.13 (6H, S)	—	8.68–6.90 (m)	−127
$Ph_2SiCl(N^{\cap}N)$	—	2.17 (3H, S)	—	8.40–6.80 (m)	−93
$Ph_2Si(N^{\cap}N)_2$	—	2.10 (6H, S)	—	8.22–7.24 (m)	−107
$Ph_3Si(N^{\cap}N)$	—	2.15 (3H, S)	—	8.14–7.10 (m)	−89

[a] m: multiplet; br: broad; s: singlet.

Table 4. ^{13}C NMR spectral data (δ, ppm) for the sulfonamide imine and its silicon complexes

Sulfonamide imine and product formed	Azomethine C atom	$Si-CH_3$	C_1 C_5	C_2 C_6	C_3 C_7	C_4 C_8
($N^{\cap}NH$)	156.9	—	146.0	139.0	121.2	144.0
			128.7	123.0	124.5	126.2
$Me_2SiCl(N^{\cap}N)$	145.7	14.1	149.7	140.2	121.3	142.9
			126.2	120.9	124.0	119.9
$Me_2Si(N^{\cap}N)_2$	150.0	15.9	147.9	140.9	121.5	143.2
			125.4	122.0	123.5	118.2
$Ph_2SiCl(N^{\cap}N)$	154.6	—	146.8	136.7	120.9	142.1
			127.2	123.0	121.4	124.0
$Ph_2Si(N^{\cap}N)_2$	147.4	—	144.9	138.0	126.9	143.5
			129.0	122.2	121.8	124.9
$Ph_3Si(N^{\cap}N)$	155.0	—	144.2	134.2	121.1	143.9
			127.9	122.3	124.0	125.0

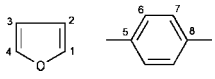

Table 5. Antifungal screening data (inhibition (%) after 96 h) for the sulfonamide imine and its silicon complexes at concentrations of 25, 50 and 100 ppm

Sulfonamide imine and product formed	Inhibition (%)											
	Aspergillus niger			*Macrophomina phaseolina*			*Fusarium oxysporum*			*Alternaria alternata*		
	25 ppm	50 ppm	100 ppm	25 ppm	50 ppm	100 ppm	25 ppm	50 ppm	100 ppm	25 ppm	50 ppm	100 ppm
($N^{\cap}NH$)	33	52	61	35	49	67	40	56	66	43	52	66
$Me_2SiCl(N^{\cap}N)$	36	54	65	38	50	68	43	58	67	45	54	68
$Me_2Si(N^{\cap}N)_2$	43	56	76	46	58	77	45	61	75	48	60	78
$Ph_2SiCl(N^{\cap}N)$	40	55	71	42	52	71	44	60	70	46	56	71
$Ph_2Si(N^{\cap}N)_2$	46	58	78	48	60	80	49	64	79	50	62	80
$Ph_3Si(N^{\cap}N)$	42	56	73	45	54	74	46	61	73	48	57	75
Bavistin	69	86	98	72	82	96	70	91	100	71	86	100

fungicidal activities, and the preliminary results achieved have led us to conclude that these types of compound should be studied in detail for their applications in diverse areas.[16]

Nematicidal activity

Ten pesticidal chemicals (Thiride, Dithane M-45, Bavistin, Aldrin 30 E.C., Monocrotophos, Thimet 10G, Furadan 3G, Phorate 10G, Ziram and Satum) were tested against *M. incognita* in testing soybean variety T-49. All the chemicals except Bavistin and Ziram were effective in reducing nematode larval population (Table 7).[20] The indirect nematostatic effects of non-fumigant nematicides resulting from impairment of neuromuscular activity, interfere with movement, feeding, invasion, development, reproduction, fecundity and hatching of nematodes are considered more important than their direct killing action; hence, much smaller amounts of non-fumigant than fumigant nematicides are needed in plant protection against nematodes.[21–23]

Insecticidal activity

The action of insecticides upsets the normal behaviour and actions of the target organisms, and the surest and quickest way to achieve this is to poison the nervous system.[24] How this upsetting is brought about and what chemical disturbances are set in, comprise the science of pharmacodynamics or pharmacology of insecticides. The routes through which the insecticides enter the body of an insect are (i) cuticle, (ii) mouth, (iii) spiracles, and (iv) other exposed sensory organs. The site of entry generally depends on the type of insecticide. Insecticides having high vapour pressure enter through spiracles or antennae. Lipophilic insecticides gain entry through the cuticle. Those insecticides that are given

Table 6. Antibacterial screening data for the sulfonamide imine and its silicon complexes (inhibition zone diameter after 24 h) at concentrations of 500 and 1000 ppm

Sulfonamide imine and product formed	Inhibition zone diameter (mm)							
	Escherchica coli (−)		*Klebsiella aerogenous* (−)		*Pseudomonas cepacicola* (−)		*Staphylococcus aureus* (+)	
	500 ppm	1000 ppm	500 ppm	1000 ppm	500 ppm	1000 ppm	500 ppm	1000 ppm
($N^{\cap}NH$)	5	6	7	10	9	12	9	14
$Me_2SiCl(N^{\cap}N)$	8	11	10	13	11	13	11	16
$Me_2Si(N^{\cap}N)_2$	11	15	12	16	15	16	14	19
$Ph_2SiCl(N^{\cap}N)$	9	13	11	14	13	15	13	17
$Ph_2Si(N^{\cap}N)_2$	11	18	13	18	17	17	17	19
$Ph_3Si(N^{\cap}N)$	10	15	12	15	14	16	14	18
Streptomycin	1	2	3	5	2	5	15	17

Table 7. Nematicidal screening data for the sulfonamide imine and its silicon complexes at concentrations of 25, 50 and 100 ppm

Sulfonamide imine and product formed	Hatching (%) in *M. incognita* after 24 h		
	25 ppm	50 ppm	100 ppm
($N^{\cap}NH$)	24.00	20.7	16.3
$Me_2SiCl(N^{\cap}N)$	21.7	17.3	nil
$Me_2Si(N^{\cap}N)_2$	20.4	16.2	nil
$Ph_2SiCl(N^{\cap}N)$	21.5	17.9	nil
$Ph_2Si(N^{\cap}N)_2$	18.8	12.8	nil
$Ph_3Si(N^{\cap}N)$	19.2	15.8	nil

with food material and those having high polarity, such as arsenicals and inorganic fluorides, enter through the mouth.[7]

Ovicidal action

It was observed that few egg shells split and few aborted undeveloped larvae which failed to come out of the eggs (Table 8). However, it was observed that some other treated eggs disfigured and stuck to the surface as a dried yellow mass without showing shell splitting. This might be suggestive that the toxic substances of the chemicals interfere in normal embryonic development, which in turn may result in certain disturbances during the process of cell division and blastokinesis, thus exhibiting impressive ovicidal properties against *Trogoderma granarium*.

Larvicidal action

High larvicidal activity was obtained with the chemicals (Table 9). It was recorded that earlier larval instars were more susceptible than the later instars, which is suggestive of the fact that chemicals penetrate easily into the larva of earlier stage cuticle. At a later stage the chemicals fail to penetrate due to more cuticularization. These chemical-treated grains were only slowly fed on or very less fed by the larvae of *T. granarium*, which leads to starvation in the developing larvae and ultimately results in their mortality.

Table 8. Ovicidal screening data for the sulfonamide imine and its silicon complexes

Sulfonamide imine and product formed	Dose level (ppm)	Average no. of eggs hatched	Average no. of eggs unhatched	Eggs hatching (%)	Eggs unhatched (%)	Corrected mortality (%)
($N^{\cap}NH$)	100	16	4	80	20	15.78
	200	12	8	60	40	38.84
$Me_2SiCl(N^{\cap}N)$	100	14	6	70	30	26.31
	200	9	11	45	55	52.63
$Me_2Si(N^{\cap}N)_2$	100	10	10	50	50	47.36
	200	7	13	35	65	63.15
$Ph_2SiCl(N^{\cap}N)$	100	11	9	55	45	42.10
	200	7	13	35	65	63.15
$Ph_2Si(N^{\cap}N)_2$	100	8	12	40	60	57.89
	200	4	16	20	80	78.94
$Ph_3Si(N^{\cap}N)$	100	10	10	50	50	47.36
	200	5	15	25	75	73.68
Control	—	19	1	95	5	—

Table 9. Larvicidal screening data for the sulfonamide imine and its silicon complexes

Sulphonamide imine and Product formed	Dose level (ppm)	Average no. of pupae formed	Average no. of dead larvae	Pupal formation (%)	Larval mortality (%)	Corrected mortality (%)
($N^{\cap}NH$)	100	16	4	80	20	15.78
	200	13	7	65	35	31.57
$Me_2SiCl(N^{\cap}N)$	100	13	7	65	35	31.57
	200	9	11	45	55	52.63
$Me_2Si(N^{\cap}N)_2$	100	10	10	50	50	47.36
	200	7	13	35	65	63.15
$Ph_2SiCl(N^{\cap}N)$	100	11	9	55	45	42.10
	200	8	12	40	60	57.89
$Ph_2Si(N^{\cap}N)_2$	100	9	11	45	55	52.63
	200	5	15	25	75	73.68
$Ph_3Si(N^{\cap}N)$	100	10	10	50	50	47.36
	200	7	13	35	65	63.15
Control	—	19	11	95	5	—

Table 10. Pupicidal screening data for the sulfonamide imine and its silicon complexes

Sulfonamide imine and product formed	Dose level (ppm)	Average no. of adults emerged	Average no. of pupae mortality	Emerged adults (%)	Pupal mortality (%)	Corrected mortality (%)
($N^{\cap}NH$)	100	16	4	80	20	15.78
	200	14	6	70	30	26.31
$Me_2SiCl(N^{\cap}N)$	100	13	7	65	35	31.57
	200	11	9	55	45	42.10
$Me_2Si(N^{\cap}N)_2$	100	11	9	55	45	42.10
	200	6	14	30	70	68.42
$Ph_2SiCl(N^{\cap}N)$	100	11	9	55	45	42.10
	200	8	12	40	60	57.89
$Ph_2Si(N^{\cap}N)_2$	100	9	11	45	55	52.63
	200	5	15	25	75	73.68
$Ph_3Si(N^{\cap}N)$	100	10	10	50	50	47.36
	200	7	13	35	65	63.15
Control	—	19	1	95	1	—

Table 11. Adulticidal screening data for the sulfonamide imine and its silicon complex

Sulfonamide imine and product formed	Dose level (ppm)	Average no. of adults in each vial	Average mortality after 48 h	Adult mortality (%)	Corrected mortality (%)
($N^{\cap}NH$)	100	20	5	25	21.05
	200	20	6	30	26.31
$Me_2SiCl(N^{\cap}N)$	100	20	6	30	26.31
	200	20	10	50	47.36
$Me_2Si(N^{\cap}N)_2$	100	20	11	55	52.63
	200	20	13	65	63.15
$Ph_2SiCl(N^{\cap}N)$	100	20	8	40	38.84
	200	20	11	55	52.63
$Ph_2Si(N^{\cap}N)_2$	100	20	12	60	57.89
	200	20	14	70	68.42
$Ph_3Si(N^{\cap}N)$	100	20	10	50	47.36
	200	20	13	65	63.15
Control	—	20	1	5	—

Pupicidal action

The pupicidal action of the chemicals (Table 10) depends on the penetration/movement of the chemicals into the puparium. After entering the puparium the chemicals disrupt the normal metabolic activities of the developing insect, interfering with metabolic activities and inhibiting development of the insect.

Adulticidal action

The chemicals applied by contact or as stomach poisons seemed to be the most hazardous for the beetles (Table 11). These chemicals, when mixed with their food, penetrate rapidly through the body wall of insects and thereby obstruct the normal respiratory activities of adults by adversely affecting the spiracles.

Acknowledgements

We are grateful to CSIR, New Delhi, India, for financial support. C. N. Deshmukh is extremely grateful to Dr Devi Singh Shekhawat, without whose blessings this work could not have been completed. C. N. Deshmukh also expresses her gratitude to Dr K. G. Khamre and Dr K. N. Patil for their encouragement throughout this work.

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